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AECU-924

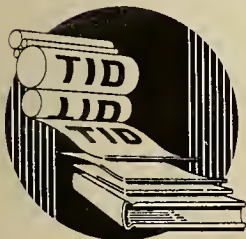
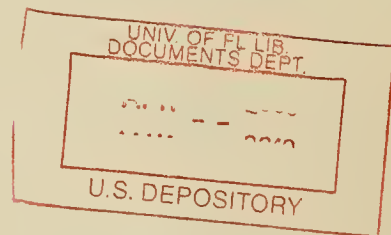
THE AUTOREDUCTION OF AM(VI) AND AM(V)  
IN DILUTE ACID

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November 10, 1950  
[TIS Issuance Date]

Los Alamos Scientific Laboratory



Technical Information Division, ORE, Oak Ridge, Tennessee

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## THE AUTOREDUCTION OF AM(VI) AND AM(V) IN DILUTE ACID\*

By L. B. Asprey and S. E. Stephanou

In various studies on the higher oxidation states of americium, it was always observed that reduction of Am(VI) to Am(V) followed by the reduction of Am(V) to Am(III) occurred. This phenomenon was investigated in order to determine the cause of this reduction and to establish a quantitative expression for the rate.

Rate studies were made, varying such factors as the hydrogen ion concentration, americium concentration, the ratio of the various ionic species of americium, and the ionic strength. The concentration of the different ionic species of americium was determined spectrophotometrically with the Model DU Beckman spectrophotometer and quartz microcells, using volumes of the order of 100  $\mu$ l. Perchloric acid solutions were used in the range 0.035 to 1.0M in all but one experiment to avoid complex ion formation. The americium used in the studies was greater than 98 per cent pure. Concentrations of americium varied from 0.008M to 0.033M. The ionic strength was adjusted by means of sodium perchlorate.

The preparation of Am(VI) was achieved by means of peroxydisulfate oxidation at about 85°C. Preparation of Am(V) was carried out using alkaline hypochlorite at ~75°C according to the method of Werner and Perlman.

When the concentration of Am(VI), Am(V), or Am(III) was plotted against time, a straight line was obtained. This indicates that the reduction is a zero order reaction with respect to the particular ionic species. Figure 1 shows that Am(VI) in 1M perchloric acid reduces to Am(V) with only a very small growth of Am(III). Am(V) increased linearly, reaching a maximum concentration when the Am(VI) was completely reduced. Then Am(V) reduced linearly to Am(III) at approximately half the Am(VI) reduction rate.

In Table 1, rates of reduction occurring at a number of different concentrations of americium are tabulated.

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\*Manuscript for a 15-minute talk given by L. B. Asprey at the Chicago meeting of the American Chemical Society on September 5, 1950, based on work performed at the Los Alamos Scientific Laboratory of the University of California.

Table 1--Experimental Results;  
Postulated Rate Law:  $-d \text{ Am(V)}/dt = k (\text{Am})$

(H)	$\mu$	Acid	Total Am, Moles/liter	Rate of change, $(M \times 10^3)$ (liter hour)		$k, (\text{Moles Am(V) Reduced})$ (Moles Am hour)	
				$-d(\text{Am(V)})/dt$	$+d(\text{Am(III)})/dt$	Am(V)	Am(III)
1.1	1.1	HClO <sub>4</sub>	0.009	0.20	0.21	0.022	0.023
1.1	1.1	HClO <sub>4</sub>	0.025	0.62	0.66	0.025	0.026
1.0	1.0	HClO <sub>4</sub>	0.033	0.70	0.73	0.021	0.022
1.0	1.0	HClO <sub>4</sub>	0.016	0.39	0.42	<u>0.024</u>	<u>0.026</u>
Average						0.023	0.024
0.5	1.1	HClO <sub>4</sub>	0.023	0.83	0.83	0.036	0.036
0.3	1.0	HClO <sub>4</sub>	0.011	0.22	0.25	0.020	0.023
0.1	0.1	HClO <sub>4</sub>	0.008	0.14	0.15	0.018	0.019
0.035	1.1	HClO <sub>4</sub>	0.009	0.15	0.15	0.017	0.017
0.1	0.3	H <sub>2</sub> SO <sub>4</sub>	0.016	0.25	0.26	0.016	0.016

It can be seen that the reduction is first order with respect to the total concentration of americium for the reduction of Am(V) to (III). At a particular hydrogen ion concentration, the values of  $k$  obtained are in fair agreement. In the one experiment in 0.5M HClO<sub>4</sub> an abnormally high value was obtained. In the experiments on the reduction of Am(VI) to Am(V), values of  $k$  were found to be 0.046 and 0.054 in 1 and 0.5M HClO<sub>4</sub>, respectively. As would be expected, these values are about twice those for the reduction of Am(V) to Am(III), since only one equivalent is involved.

These results suggest that the reduction of Am(VI) to Am(V) followed by the reduction of Am(V) to Am(III) is caused by the Am<sup>241</sup> alphas reacting with the water. Probable reductants formed by the reaction of alphas with water are H<sub>2</sub>O<sub>2</sub> and H atoms but other fragments may be involved. Throughout the reduction, gas was evolved from the americium solutions but no determination of the amount or composition of the gas has been made in the present study.

The variation in the rate constant may be due in part to a small effect of the hydrogen ion concentration. Probably a more important factor is the variation between solutions due to small amounts of adventitious impurities which decompose the reducing agent or change the degree of recombination of the water fragments.

If the products of the alpha radiation of water cause this reduction, then the rate of reduction should be a function of the americium half-life and the energy of its alpha radiation. A calculation showing the number of electron volts available from alpha radiation in terms of one equivalent of Am(V) reduced to Am(III) is given herewith.

Calculation of the number of ev/molecule of Am(V) reduced by 1M HClO<sub>4</sub>

d/m/g of Am	At. Wt. of Am	d/m/to d/hr	ev/alpha from Am <sup>241</sup>	ev/mole Am/hr
$7 \times 10^{12}$	241	60	$5.47 \times 10^6$	$= 5.55 \times 10^{23}$
<hr/>				
$5.55 \times 10^{23}$			$\frac{\text{ev}}{\text{mole Am} - \text{hr}}$	$= 38 \text{ ev/molecule Am(V) reduced to Am(III) or 19 ev/per equivalent}$
$0.024^* \times 6.02 \times 10^{23}$			$\frac{\text{molecules Am(V) reduced}}{\text{mole Am} - \text{hr}}$	

\*Average value of k from four experiments in 1M HClO<sub>4</sub>

A summary of the results appears in Table 2. The value of 19 ev obtained in 1M HClO<sub>4</sub> agrees well with the value of 20 ev found by Duane and Scheuer in experiments using radon as the alpha source. However, the values found by a number of investigators cover the range from 20 to 80 ev.

Table 2--Electron Volts per Equivalent of Am(V) Reduced

(H+)	$\mu$	Acid	ev/equivalent Am(V) reduced	ev/equivalent Am(VI) reduced
1.1	1.1	HClO <sub>4</sub>	20	
1.0	1.1	HClO <sub>4</sub>	18	20
1.0	1.0	HClO <sub>4</sub>	21	
1.0	1.0	HClO <sub>4</sub>	18	
0.5	1.1	HClO <sub>4</sub>	13	17
0.3	1.0	HClO <sub>4</sub>	21	
0.1	0.1	HClO <sub>4</sub>	25	
0.035	1.1	HClO <sub>4</sub>	27	
0.1	0.3	H <sub>2</sub> SO <sub>4</sub>	29	

The reduction of Am(VI) and Am(V) is zero order with respect to the species being reduced and first order with respect to the total americium concentration. These results can be satisfactorily explained as due to the reaction of the americium alpha particles with water. Since other workers have found H<sub>2</sub>O<sub>2</sub> to be a principle product of the reaction between alpha particles and water, this offers a reasonable explanation for the reduction observed. No direct experiments have been made to determine whether a hydrogen peroxide mechanism is involved.



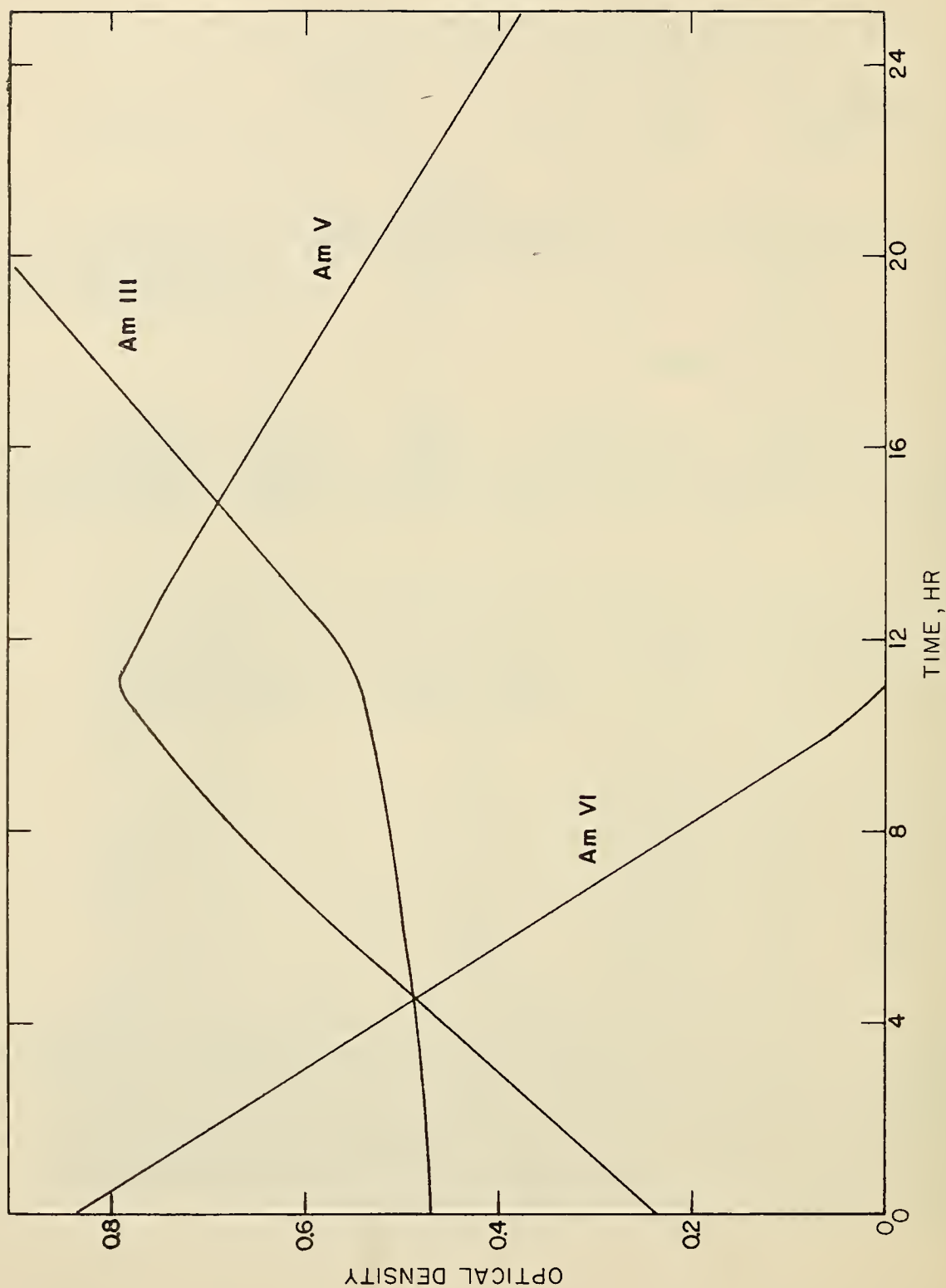
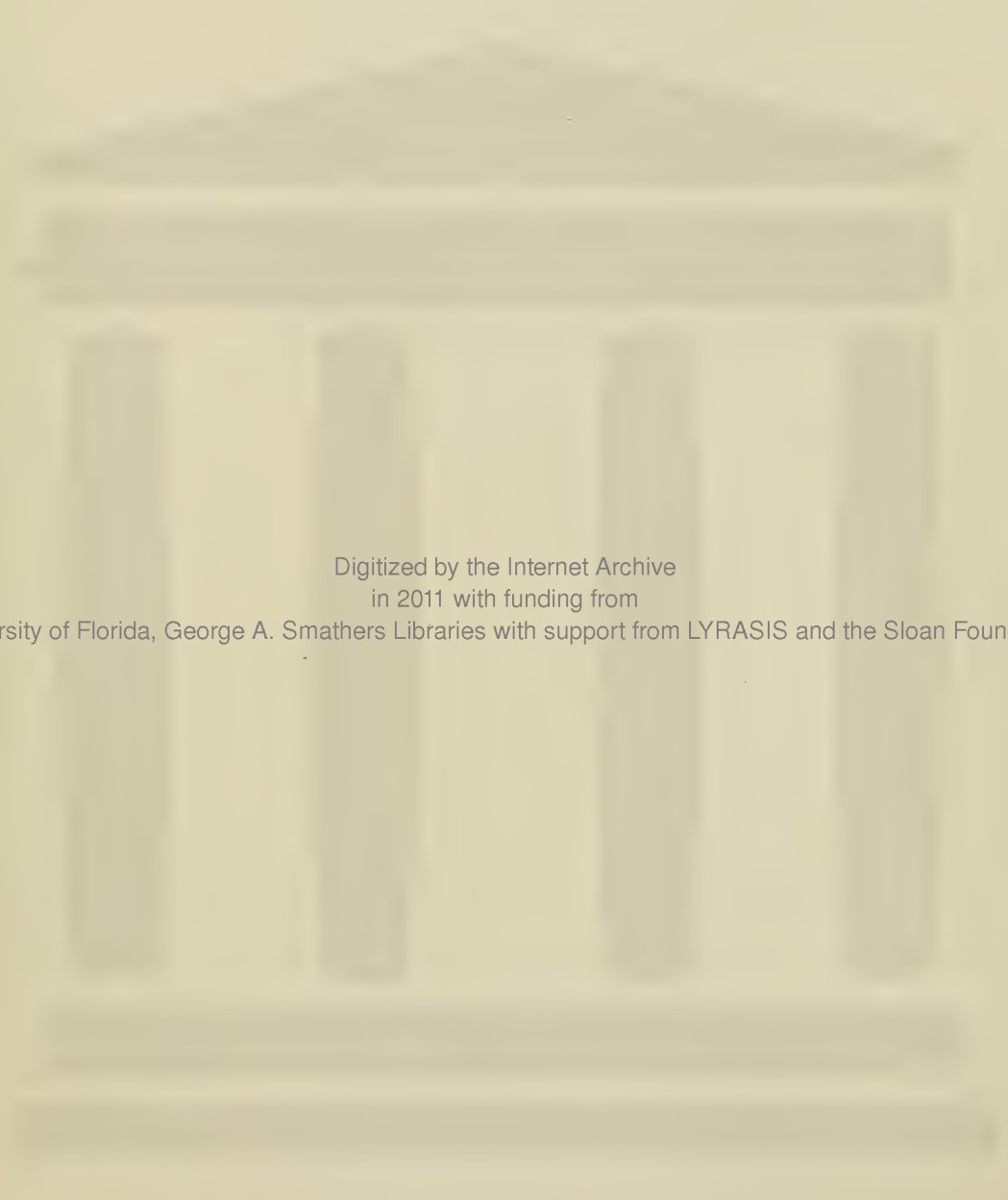


Fig. 1--Curves showing the optical densities of Am(VI), Am(V), and Am(III) absorption peaks plotted against time for the auto-reduction of Am(VI) and Am(V) in 1.0M HClO<sub>4</sub>.



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